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**ON THE MOLECULAR-ORBITAL THEORY OF CONJUGATED
ORGANIC COMPOUNDS WITH APPLICATIONS
TO THE PERTURBED BENZENE RING***

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ABSTRACT

The electronic structure of a molecular system is investigated by using the idea of molecular orbitals. The behaviour of the separate molecular orbitals and the orbital energies under the influence of the substitution of one or more heteroatoms, considered as perturbations, is examined. A series of quantities, separate charge orders, bond orders, and mutabilities are introduced, giving information about some characteristic physical and chemical properties of the compound. The perturbation scheme is carried out explicitly to the second order in the energies and to the first order in the orbitals, and special attention is paid to the treatment of degenerate levels. The overlapping problem is fully discussed. The basic results are independent of any empirical parameters, and they may be used either in the naive semi-empirical theory or in a more elaborate theoretical approach based on an antisymmetrized molecular wave function.

As an example, numerical applications are carried out in detail on benzene. Separate charge orders, bond orders, and mutabilities are tabulated, and orbital energies for a perturbed benzene ring with one or two heteroatoms are explicitly given.

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Absorption Studies of the Vapors of the Three Isomeric
Picolines in the Near Ultraviolet.* +

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Abstract

Studies of the near ultraviolet absorption spectra of α -, β -, and γ -picoline vapor have been made in low and medium dispersion. Conclusive evidence is found for two electronic transitions in the vicinities of 35500 and 38500 cm^{-1} . The former transition is interpreted as an allowed A_1-B_2 transition resulting from the excitation of an sp^2 non-bonding electron of the nitrogen atom into the first unfilled π orbital of the ring. The latter transition is considered an allowed A_1-B_1 transition resulting from the excitation of a π ring electron. The A_1-B_2 system exhibits narrow headless bands similar to the first absorption bands in pyridine. It is of weak intensity comparable to that of the forbidden $A_{1g}-B_{2u}$ transition in benzene. The A_1-B_1 system, which is much stronger, consists of broad diffuse bands. There is evidence that this system may be overlapped by another transition in β -picoline.

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+ Based in part on a dissertation by J. H. Rush submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University, 1950.

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Introduction

In recent years a number of spectroscopic studies in the near ultraviolet have been published for the vapor phase of simple aromatic molecules consisting of a benzene ring with single and multiple substitutions of atoms or simple groups for an H atom in the ring. A logical further step has been to study spectroscopically the effect of a substituent in the carbon ring itself, as in pyridine (C_5H_5N), and also to compare the effects of a given substituent replacing an H atom in benzene and in pyridine.

The analysis of the near ultraviolet absorption spectrum of pyridine was undertaken by Henri and Angenot in 1935¹, and later by Sponer and Stäcklen.^{2,3} In the latter publications it was assumed that the excitation in pyridine is caused by the 2π electrons of the ring as in benzene. The treatment leads to an electronic level of symmetry type B_1 as first excited singlet in pyridine. The molecule itself belongs to symmetry group C_{2v} . These analyses were not entirely satisfactory. It was hoped that a study of simple pyridine derivatives would yield information which would also be of significance in the analysis of pyridine. The picolines (methyl-pyridines $C_5H_4N.CH_3$) were chosen for the present study. Apparently no data on their ultraviolet absorption spectra in the vapor phase had been published since some early exploratory studies,^{4,5} when this research

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 2. H. Sponer, *Rev. Mod. Phys.* 16, 224 (1944).
 3. H. Sponer and H. Stäcklen, *J. Chem. Phys.* 14, 101 (1946).
 4. F. Baker and E.C.C. Baly, *J. Chem. Soc.* 91, 1122 (1907); J. E. Purvis, *J. Chem. Soc.* 95, 294 (1909); *ibid.* 97, 692 (1910); E. Herrmann, *Zeits. f. wiss. Phot.* 18, 253 (1919).
 5. We are indebted to Drs. J. Duchesne and L. d'Or for such data for α -picoline, from the Ph.D. dissertation of P. Angenot at Liege in 1936.

was carried out. A preliminary report on our experimental findings was published.⁶ It was learned that at the same time the near ultraviolet absorption spectrum of pyridine was being reinvestigated at M.I.T. with large dispersion together with a study of the corresponding absorption in completely deuterated pyridine.⁷ Recently Herington,⁸ in a paper on the use of the electronic spectra of pyridine homologues for quantitative analysis, has reported a number of absorption bands in the vapors of all three picolines. He has also taken the spectra in non-polar and polar solutions. Similar measurements had been carried out in this laboratory.⁹ Absorption curves of α -picoline in isooctane may also be found in the catalog of Ultraviolet Spectrograms.¹⁰ Raman and infrared frequency values for α - and β -picolines have been well established by Jatkar,¹¹ Manzoni-Ansidei,¹² Kohlrausch and coworkers,¹³ Lecomte,¹⁴ and others. On the spectrum of γ picoline apparently the only published information¹⁵ in this region is a curve of absorption in the region 800 - 2000 cm^{-1} .

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13. E. Herz, L. Kahovec and K.W.F. Kohlrausch, J. physik. chem. B53, 124 (1943).
14. J. Lecomte, Compt. Rend. 207, 395 (1938); J. Phys. et Rad. 9, 512 (1938).
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Experimental Procedures.

Samples of α -picoline 99.85% pure (b.p. 129.44°C) and β -picoline 99% pure (b.p. of fraction 143.0 to 143.5°C) were supplied by Dr. J. J. McGovern of the Mellon Institute of Pittsburgh. The γ -picoline was from a lot purified (b.p. of fraction 144.5 to 145.0°C) by Dr. J. C. Shivers of the Department of Chemistry of Duke University, and redistilled by us.

Some preliminary studies on the medium Hilger quartz prism spectrograph were made using three short fused quartz cells. Most of the final measurements of the long-wavelength portion of each spectrum were made from plates taken in the first order of a 3m grating spectrograph. In this latter series a single 75 cm quartz cell was used. Each cell was provided with a reservoir tube for taking the substance.

The spectra were obtained in dependence of the vapor pressures of the substances by varying the temperature of the substance in the cell reservoir. This procedure of course, has the disadvantage that changes in concentration necessarily involve changes in the degree of thermal excitation of vibrational levels in the ground state of the molecule, since the cell temperature must equal or exceed that of the reservoir to prevent condensation in the cell. But the effects of pressure changes and excitation changes can usually be disentangled to some extent, particularly when plates taken with cells of different lengths are compared. Temperature control was effected by using two separate electrical ovens for the absorption tube and the reservoir arm, the latter always being 2 to 5 degrees cooler than any other part of the cell. In working below room temperature, the cell was customarily left at room temperature while the reservoir was immersed in suitable coolants in a small Dewar flask.

The pressures corresponding to the various cell temperatures were evaluated from the data on pyridine and picoline vapor pressures already in the literature. The vapor pressures of α -picoline were obtained from a plot of Riley and Bailey's¹⁶ values, which extended down only to 6 mm (16°C). The vapor pressure of β -picoline and γ -picoline was determined at 0° and 20°C by Brown and Barbaras.¹⁷ Extension to lower and higher values was obtained by Dühring's rule from the normal boiling points of these compounds and from the vapor pressure data on pyridine given by van der Meulen and Mann.¹⁸ For low pressures below 1 mm new data were used, obtained¹⁹ on all three picolines in this laboratory.

The optical arrangement was of the conventional type. A low-voltage d.c. hydrogen discharge lamp, watercooled, was used with the Hilger instrument, and a high voltage lamp (0.7 Amp. at 2200 volts) with the grating spectrograph. A Corning "red purple Corex A" Nr. 9863 filter, passing the region 2400 to 4000 Å, was put in front of the source in most exposures. Iron lines were used as the comparison spectrum. Exposure times on the Hilger instrument were about one minute while they ranged on the grating spectrograph from 20 minutes to 2 hours.

It was found that the spectra consist of a long-wavelength portion of low intensity exhibiting narrow, headless bands and a short-wavelength portion of higher intensity with broad, diffuse bands and with a steep absorption gradient in the region where the portions

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17. H. C. Brown and G. K. Barbaras, J. Am. Chem. Soc. 69, 1137 (1947).

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overlap. Eastman III-O emulsion was found to be best suited for most of the pipeline research.

The narrow bands of the long-wavelength region exhibit no clear-out band heads, but are like the narrow, diffuse-edged bands of pyridine. It seemed therefore most practicable to measure to the most intense region of the band, recognizing that the relation of this setting to the true rotationless frequency of the band must be uncertain and probably variable. Uncertainties in the resulting values range up to 10 wavenumbers.

The bands of the short-wavelength region are so diffuse that it was found best to measure them on photographic prints of the Hilger prism spectrograms enlarged about 5 times. Since the frequency dispersion of the prism is nearly linear in the region concerned, uncertainties in locating the diffuse bands were within 10 to 100 cm^{-1} .

Experimental Results.

As mentioned before, the relative intensities in the long wavelength and short wavelength parts of the spectrum which we call regions I and II, differ markedly. Region I with its narrow pyridine-like bands occurs at about 2900 - 2700 Å. Region II occurs at about 2700 - 2400 Å and its diffuse broad bands resemble the spectra of some substituted benzenes. No attempt was made to determine intensities quantitatively. It is possible, however, to obtain a rough estimate of the relative intensities of the two regions by observing at what temperature each spectrum first appears in a cell of given length. For this purpose the expression for the extinction coefficient was combined with the approximately valid assumption that the ideal gas law holds for the vapor. Adjusting then the conditions of pressure, temperature, and length of light path for the

two absorption regions so, that they exhibit the same absorption intensity, an expression was obtained from which their relative absorption may be roughly estimated. The intensity so obtained showed that the I spectra of the picolines are of the same order of intensity and that the II spectra diminish in intensity going from α - over to γ -picoline. This is in agreement with recent research²⁰ in which separate f values for the two regions were obtained from solution spectra.

The appearance of the I spectra may be seen from Fig. 1-3 which are assembled from sections of the respective spectra taken under various conditions. Spectrograms of the II spectra are reproduced in Fig. 4. The diffuse bands of the II spectra occur in three major groups of bands, of which the middle group is strongest. These groups have nearly the same position in the spectra of α - and β -picoline, with their maxima at about 38600 and 38400 cm^{-1} respectively. The band groups are not clearly differentiated in the vapor of γ -picoline; but the maximum is shifted to about 39300 cm^{-1} , and in solution three distinct peaks appear at nearly the same positions as those in pyridine solution.

The observational data for the picoline spectra are listed in Tables I - VI. Each table includes in the first column the wavelength, measured to the most intense part of the band, in the second column the wavenumber and in the third column the separation of each band from the assumed 0,0 band. Column four contains visual estimates of relative intensities. It is divided into two sub-columns giving intensity estimates under conditions stated in these columns. Notations used are: vw - very weak, w - weak, nw - medium weak, ms - medium strong, s - strong, vs - very strong, d - diffuse, r - apparently degraded to the red. The last column gives assignments

20. H. P. Stephenson, Ph.D. Thesis, Duke University, 1952.

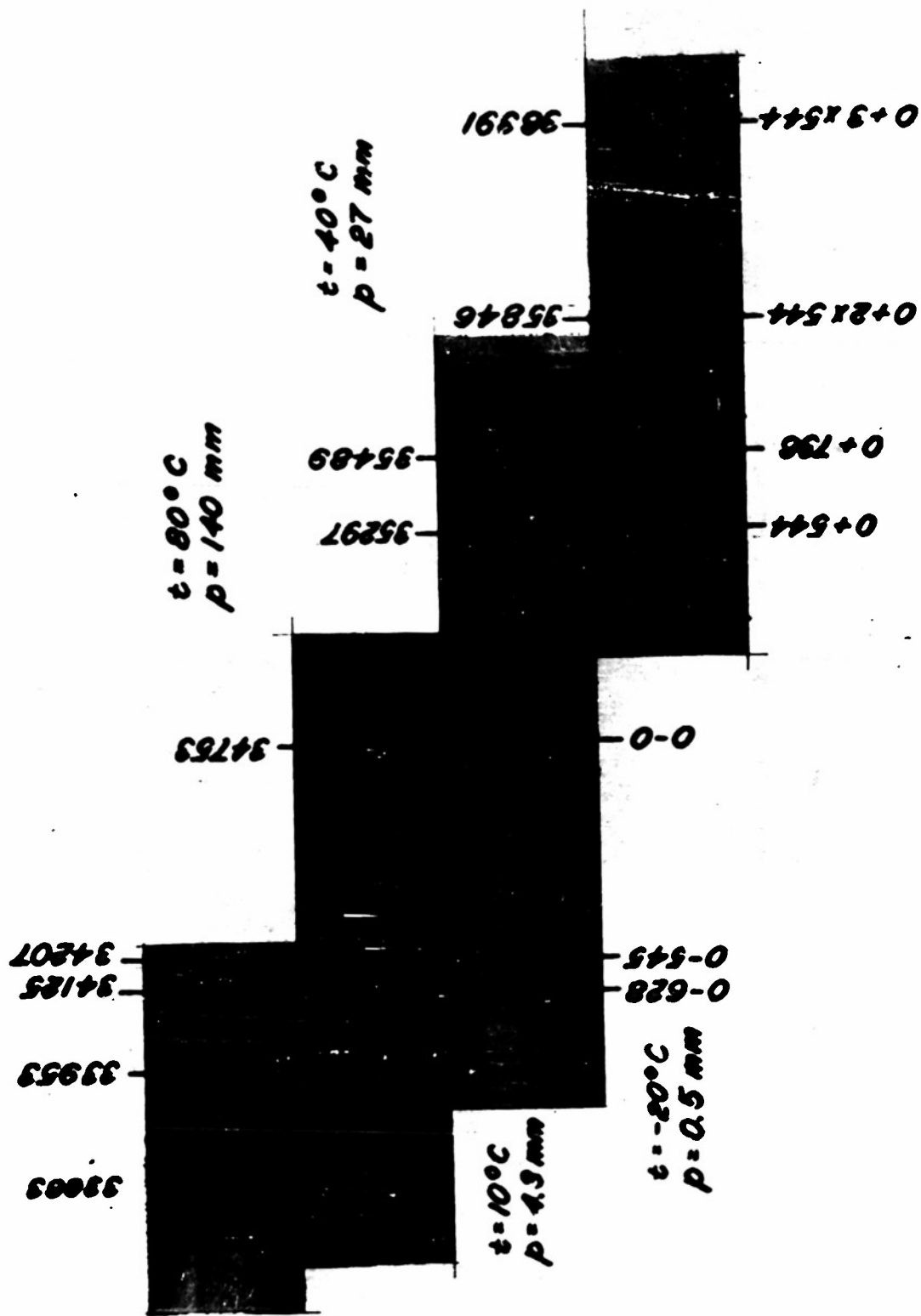


Fig.1. Spectrum of transition I in α -picoline taken in 75 cm cell.

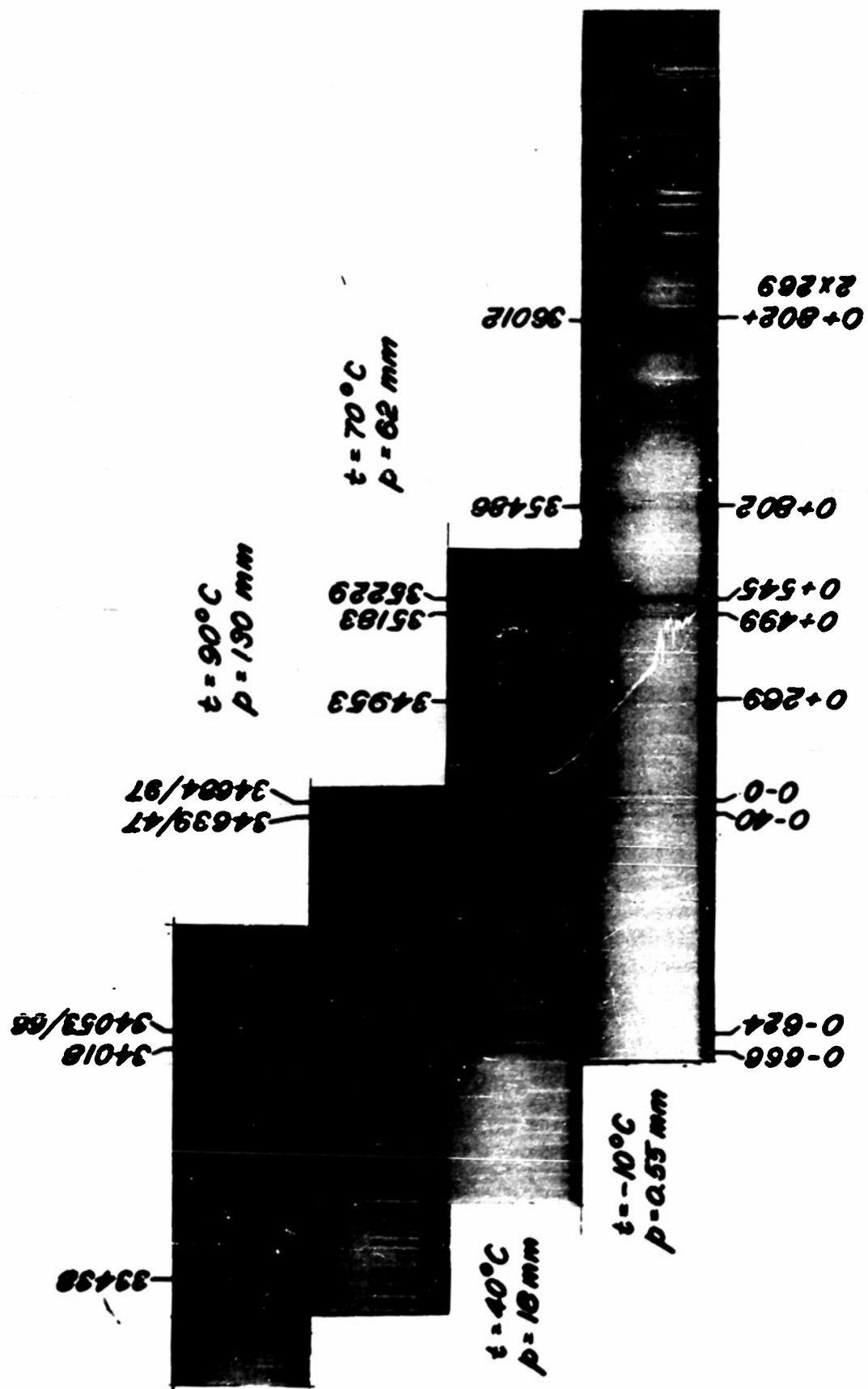


Fig.2. Spectrum of transition I in β -picoline taken in 75 cm cell.

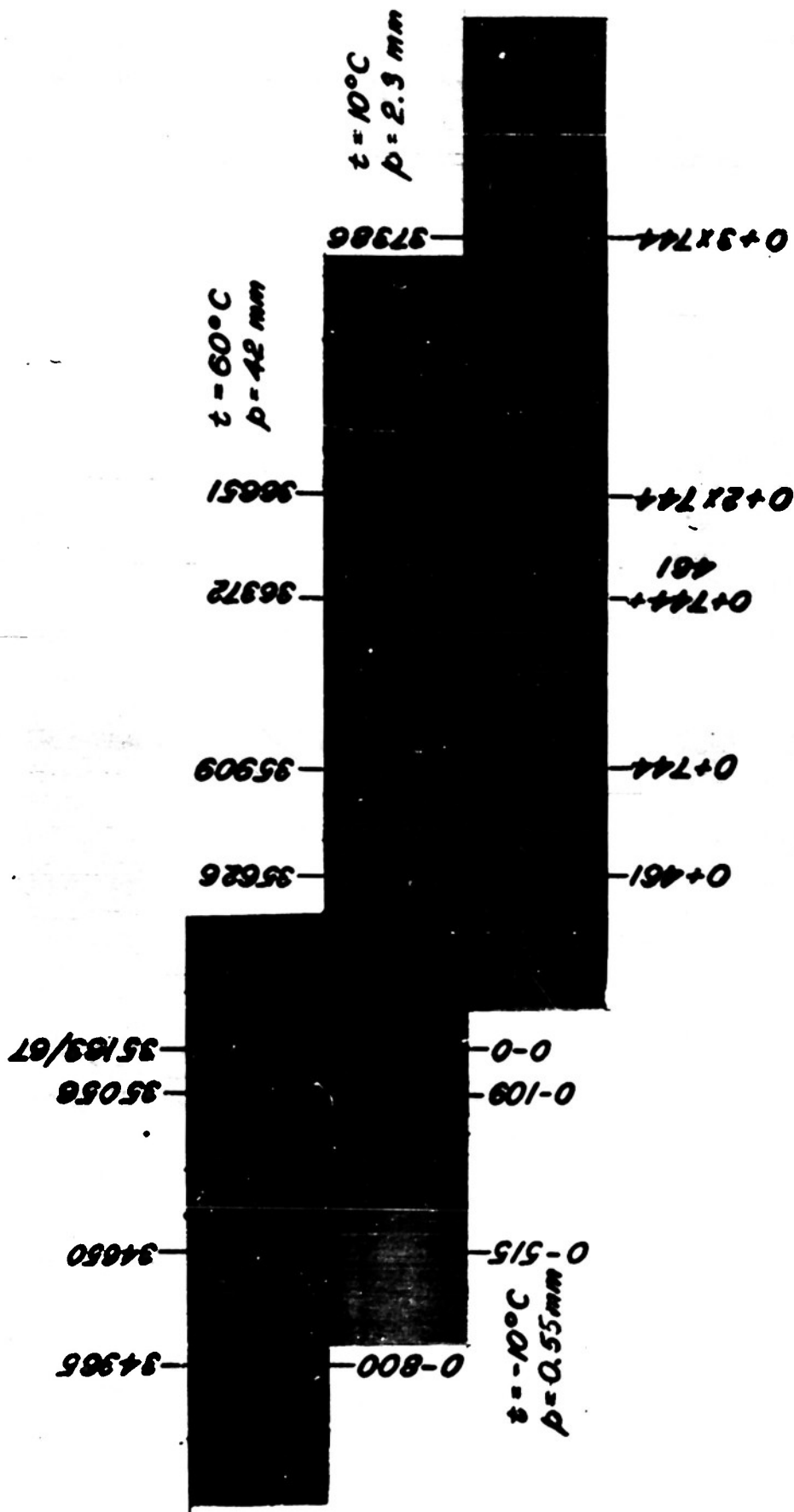


Fig.3. Spectrum of transition I in γ -picoline taken in 75 cm cell.

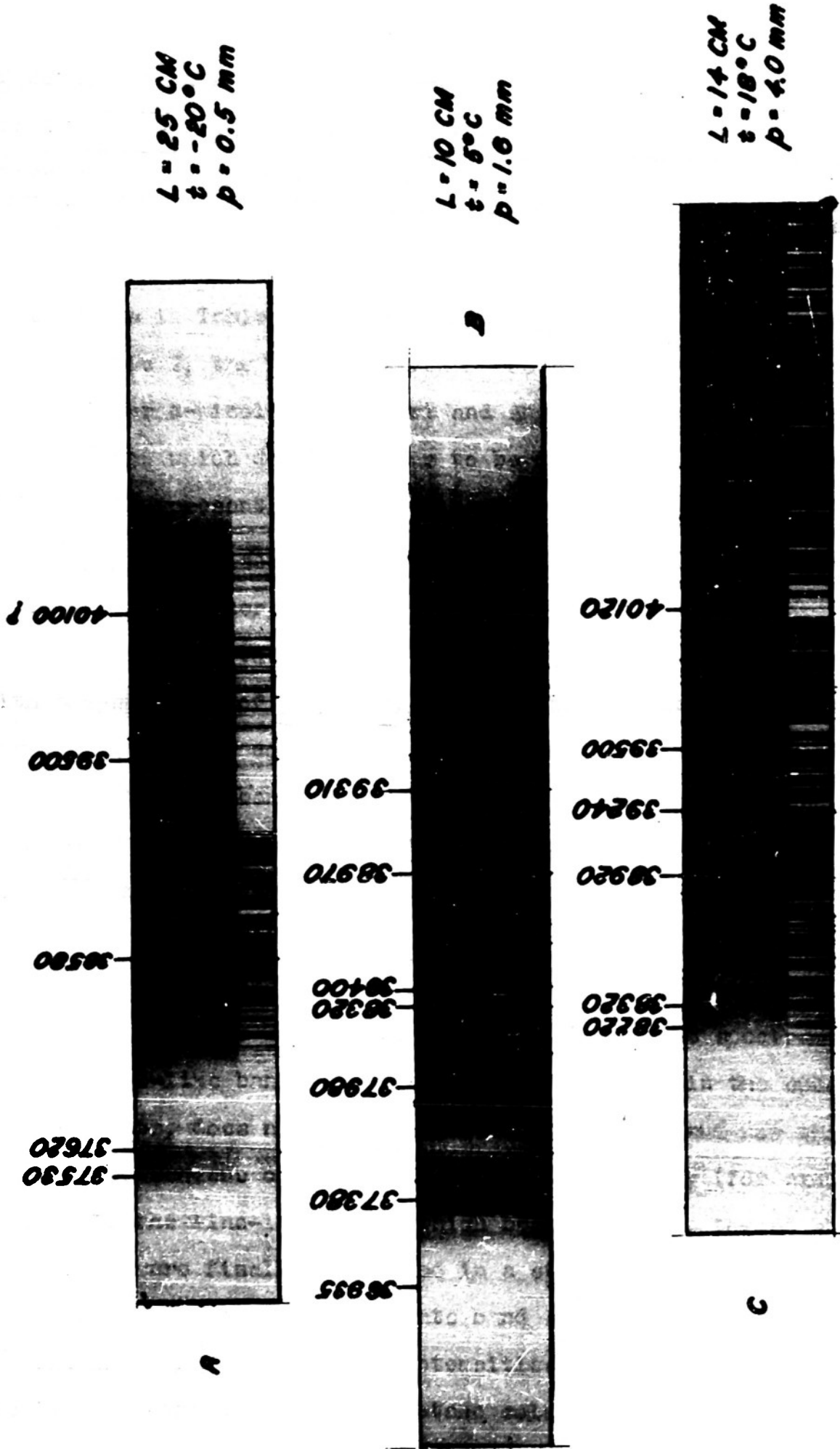


Fig. 4. Spectra of transition II.
 A: α -picoline, B: β -picoline, C: γ -Picoline.

of component vibrational frequencies of each band, by means of analysis to be detailed later. () indicates a frequency which is itself unassigned. ? indicates a doubtful assignment.

This column arrangement is modified slightly to allow for only one column of intensity estimates in Tables IV - VI and for alternate assignments in Table V.

In Table I, the starred wavenumbers are taken from the results obtained for α -picoline by Henri and Angenot.⁵ Only those values are included which do not appear to be duplicated by any value derived from the present research.

Discussion and Analysis of the Spectra

General remarks on the electronic levels.

In discussing the picoline spectra it is logical to compare them with the spectrum of pyridine, just as the spectra of substituted benzenes have been compared to that of benzene. The first electronic transition in benzene, of type $^1A_{1g} - ^1B_{2u}$ and forbidden, becomes an $A_1 - B_1$ and allowed in simple monosubstituted benzenes, when the D_{6h} symmetry of benzene is reduced to the group C_{2v} upon substitution. The same type transition, $A_1 - B_1$, would apply to pyridine if the first excitation were caused by the $2p\pi$ electrons of the ring as in benzene, as mentioned in the Introduction. Now the pyridine spectrum with its narrow, line-like bands distributed rather evenly in the spectrum and not in groups, does not resemble the benzene spectrum nor that of a substituted benzene as has been remarked previously (for example ref. 3.). While the line-like bands which become diffuse toward shorter wavelengths are finally submerged in a strong continuous background, the picolines exhibit two separate band systems of distinctly different patterns and of different intensities as described earlier. The picoline spectra taken in iso-octane solution by Stephenson⁹ in a

Table I. Absorption bands in transition I of α -picolino.

λ (Å)	ν (cm ⁻¹)	$\nu - \nu_0$	Intensity		Assignment
L=75 cm t=80°C p=140 mm					
2977.2	33579	+1174	wd		
69.7	663	-1090	vwd		0-2x545 0-1100
51.4	872*	- 881			0-887
50.8	879	- 874	vwd		
t=60°C p=66 mm					
45.6	939	- 814	vwd	vwd	0-813
44.4	953*	- 800			0-800
t=40°C p=27 mm					
29.5	34125	- 628	w	nwr	0-628
28.8	134	- 619	vw		
22.5	207	- 546	n	s	0-545
21.8	215	- 538	vw	w	
19.3	245	- 508		vw	0+120-628 0+207-2x358
18.2	258	- 495		vw	
15.5	289	- 464	wd	nsd	
06.1	400	- 353	wd		0-358
05.5	407	- 345	wd		
04.4	420	- 333	vwd		0+207-545 ?
L=25 cm t=60°C p=66 mm					
2899.2	482	- 271	wd	vw	0+355-628 0+544-813
96.3	517	- 236	vwd		0+120-358

Tablo I (continued)

λ (Å)	ν (cm ⁻¹)	$\nu - \nu_{O-O}$	Intensity		Assignment
94.7	536	- 217	vwd	vw	
93.4	552	- 201	wd		0-204
92.3	565	- 188	wd	vw	0-188 ?
88.2	613	- 140	nwr	w	
86.4	635	- 118	vwd	vw	
83.6	669	- 84	wd	vw	0-84; 0-2x42? 0+544-628; 0+120-204
80.1	711	- 42	vwd	vw	0-42
L=75 cm t=20°C p=8.0 mm					
76.6	753	0	var	sr	0-0
76.0	760	7	n		
72.4	804*	51			
70.1	832	79	nw	nw	
69.5	839	86	w		
69.1	844	91	wd		
66.7	873	120	nr	w	0+120
64.3	903*	150			0+355-204
L=75 cm t=10°C p=4.3 mm					
62.9	920	167		vw	
61.4	938	185	w	vw	0+544-358
59.6	960	207	ns		0+207
56.5	998*	245			0+2x120
55.8	35006	253	wr		
55.0	016	263	vwd		
54.0	028	275	vwd		0+355-84

Table I (continued).

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu - \nu_{0-0}$	Intensity		Assignment
51.0	065	312	nd		0+355-42
50.0	078	325	mwd		0+120+207
49.1	089	336	wd	vwd	0+544-204
47.8	105	352	nd		0+355
$t=0^{\circ}\text{C}$ $p=2.1 \text{ nm}$					
44.5	146	393	vwd		0+207+544-358
40.9	190	437		vwd	
39.3	210	457		wd	0+544-84
36.1	250	497		vwd	582-84
32.3	297	544	sr	vs	0+544
31.7	304	551		w	
29.2	335	582	w	vw	0+582
26.8	365	612	vwd	vw	0+355+544-84-204 ?
24.4	395	642	wr	w	
17.0	489	736	ndr	msdr	0+736
$L=25 \text{ cm}$ $t=20^{\circ}\text{C}$ $p=8 \text{ nm}$					
12.9	540	787		vwd	0+582+207
10.7	568	815		vwd	0+355+544-84
07.1	614	861	w	w	0+861 ? 0+736+120 0+355+544-42
03.8	656	903	w	vw	0+355+544 0+952-42
2799.9	705	952	w	vw	0+952 ?
95.7	758	1005	vw	vwd	0+2x544-84
92.0	805	1052		vwd	0+2x544-42

Tablo I (continued).

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu-\nu_{0-0}$	Intensity		Assignment
88.8	846	1093	msr	ms	0+736+355 0+2x544
83.7	912*	1159			
82.8	924	1171		nwd	0+1052+120 ?
78.8	975	1222		wd	
74.8	36027	1274		nd	0+3x544-358 ? 0+736+544
71.0	077	1324		vwd	0+582+736
67.6	122	1369		vwd	
64.4	163	1410		wd	0+355+2x544-42 ?
61.7	199	1446		wd	0+355+2x544
57.0	260	1507		wd	
$L=25\text{ cm}$ $t=10^{\circ}\text{C}$ $p=4.3\text{ mm}$					
54.3	296	1543	wd	wd	
51.6	332	1579	vwd	vwd	
49.9	354	1601	vwd	vwd	0+3x544-42
47.1	391	1638	nwd	nwd	0+3x544
41.8	461	1706	nwd	nwd	
37.2	522	1769	nwd	nwd	

* Unpublished data of Henri and Angenot.

Table II. Absorption bands in transition I of β -picolino.

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu-\nu_0$	Intensity		Assignment
$L=75 \text{ cm}$ $t=100^\circ\text{C}$ $p=190 \text{ mm}$					
3030.7	32986	-1698	vw		
26.0	33037	-1647	vwd		
2994.2	388	-1296	m		
91.2	421	-1263	vw		0-1263
89.7	438	-1246	mw		0-2x624
$L=75 \text{ cm}$ $t=80^\circ\text{C}$ $p=90 \text{ mm}$					
88.3	454	-1230	vw	vw	
85.8	482	-1202	vw	vw	
84.4	498	-1186		vw	
81.3	532	-1152	w	vw	0-1154 ?
79.3	555	-1129		vwd	
77.6	574	-1110		vwd	0-1099 ? 0-1034-2x40 ?
$t=70^\circ\text{C}$ $p=60 \text{ mm}$					
73.8	617	-1067	w	mw	0-1034-40 0-2x535
73.0	626	-1058		vw	
70.8	651	-1033)		vw	
70.4	656	-1028)	vw	vw	0-1034
69.5	666	-1018	vw	mw	
68.8	674	-1010		vw	0-2x490-40

Table II (continued)

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu-\nu_{\text{O-O}}$	Intensity		Assignment
65.2	715	- 969		vw	0-2x490 ?
63.6	733	- 951		vw	
61.3	759	- 925		vwd	
60.2	772	- 912		vwd	
59.0	785	- 899		vwd	
53.9	844	- 840	vw	vw	0-800-40
52.8	856	- 828		vw	
51.7	869	- 815		vw	
50.8	879	- 805	vw	vw	0-800 0-714-2x40
47.0	923	- 761	vwd	vw	0-714-40 ?
43.1	968	- 716	vw		0-714
39.4	34010	- 674	vw		0-2x338
t=40°C p=16 mm					
38.8	018	- 666	sr	n	0-666 0-624-40
37.9	028	- 656	vw		0-535-3x40
35.7	053	- 631)	nd	vw	0-624
34.6	066	- 618)	nsr	vw	
34.0	073	- 611	vw	vw	0-535-2x40
33.2	082	- 602	vw	vw	
30.7	112	- 572	nsr	w	0-535-40 0-490-2x40
27.6	147	- 537	vwd	vw	0-535

Tablo II (continued)

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu \cdot \nu_{0-0}$	Intensity		Assignment
26.4	161	- 523	nd	nwd	0-490-40
24.3	186	- 498	vwd	vw	0-490
23.0	201	- 483			
20.0	237	- 447			
18.5	254	- 430		vwd	
13.2	316	- 368		wd	0-2x215
12.4	326	- 358		w	
10.1	353	- 331		w	
04.6	418	- 266		vwd	0-338
03.1	436	- 248		nwd	
01.5	455	- 229		vwd	0-215-40
$t=20^{\circ}\text{C}$ $p=4.6 \text{ mm}$					
2899.9	474	- 210	wr	n	0-215
98.7	488	- 196		vw	0-198
98.1	495	- 189	vw	nw	
97.2	606	- 178	w	n	
93.5	550	- 134	vwd	w	
92.5	562	- 122			
90.8	583	- 101		vwd	
89.3	600	- 84	vwd	nwd	0-84; 0+131-215
87.5	622	- 62		nw	
86.1	639	- 45	vw	vw	0-40; 0+158-198
85.4	647	- 37			

Table II (continued)

λ (Å)	ν (cm ⁻¹)	$\nu - \nu_{0-0}$	Intensity	Assignment
84.8	655	- 29	vw	
82.3	684	0	vs	0-0
81.3	697	13	ms	
80.8	702	18	mw	0+269-3x84
80.4	708	24	w	
79.8	714	30	vw	
77.4	743	59	vwr	
75.1	771	87	vwd	
t=0°C p=1.1 mm				
73.7	788	104	mwr w	0+269-2x84 ?
71.5	815	131	vwd	0+131
69.3	842	158	vwd	0+158
67.5	864	180	wd vwd	0+269-84
61.1	941	257	mwd vw	
60.2	953	269	sr ms	0+269
57.6	984	300	nd mwd	
54.8	35019	335	vwd vwd	
52.1	052	368	vwd vwd	
50.0	078	394	vwd vwd	
42.3	093	409	vwd vwd	
46.7	128	444	vwd vwd	
43.1	163	479		
42.1	175	491	vwd	0+545-65 ?

Table II (continued)

λ (Å)	ν (cm ⁻¹)	$\nu - \nu_{0-0}$	Intensity		Assignment
			t=-10°C p=0.6 mm		
41.5	183	499	w	m	0+499
40.8	191	507	w	mw	0+545-40
40.2	199	515		w	
38.6	219	535		mw	0+2x269
37.8	229	545	mw	sr	0+545; 0+580-40
36.7	242	558		mw	
34.9	264	580	vwd	w	0+580
34.1	275	591		w	
33.2	286	602		vw	
30.9	314	630		vwd	
28.6	343	659		w	
26.4	371	687		vw	
23.7	405	721		w	
22.5	420	736		w	
18.3	472	788		w	0+802 0+3x269 ?
17.2	486	802	mr	vs	
14.2	524	840	vwd	w	
10.9	566	882		w	
09.1	588	904		w	0+2x180+545
04.7	644	960	vwd	mw	0+960 ?
01.3	688	1004	vw	mw	0+2x499; 0+1004
2799.8	706	1012		vw	
					0+2x545-84

Table II (continued)

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu - \nu_{\text{O-O}}$	Intensity		Assignment
98.7	720	1036	w	mw	
96.7	754	1070	wd	ms	0+802+269
96.0	765	1081		vw	0+545+2x269
95.2	776	1092	vwd	vw	0+2x545
92.9	794	1110	vwd	mw	
90.7	822	1138	vwd	w	
85.2	893	1209		vw	
80.9	949	1265	wd	ms	0+802+545-84 ?
79.2	971	1287	vwd		
76.0	36012	1328	wd	wd	0+802+2x269
72.7	055	1371	vwd	vw	
68.2	114	1430	vwd	w	
63.1	180	1496	wd	w	0+3x499
59.7	225	1537	wdr		0+802+545+269-84 ?
55.6	279	1595	vwd		0+2x802
51.0	340	1656	vwd		
46.0	405	1721			0+802+2x545-2x84 ?
40.9	473	1789	vwd		Transition II ?
32.5	586	1902	vwd		
28.0	646	1962	vwd		

Table III. Absorption bands in transition I of γ -picolino.

λ (Å)	λ (cm ⁻¹)	$\nu - \nu_0$	Intensity		Assignment
L=75 cm t=80°C p=85 mm					
2913.8	34310	- 855	vw		
11.9	332	- 833	vw		
18.7	352	- 813	vw		
t=60°C p=42 mm					
09.1	365	- 800	w	mw	0-800
07.9	379	- 786	vw		
06.1	400	- 765	vw		
2897.8	499	- 666	vw		
86.2	638	- 527	vw		
t=40°C p=15 mm					
85.2	650	- 515	mw	wdr	0-513
84.8	654	- 511	w		
76.7	752	- 413	vw		0-413 ?
75.1	771	- 394	vw		
73.1	806	- 359	vw		0-359 ?
69.6	838	- 327	vw		
67.2	867	- 298	vw		
65.2	892	- 273	w	w	0-273 ? 0+245-513 ?
63.2	916	- 249	vw		
60.3	951	- 214	vw		0-214
57.0	992	- 173	vw		

Tablo III (continued)

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu - \nu_0$	Intensity		Assignment
$t=30^{\circ}\text{C}$ $p=8 \text{ mm}$					
51.8	35056	- 109	vw	wr	0-109
45.8	129	- 36	w		
45.0	140	- 25	vw		
44.1	151	- 14	mw	vw	
43.1	163}	0	s	mw	0-0
42.8	167}		s	mw	
41.1	188	23	vwd		
38.8	216	51	vwd		
$t=20^{\circ}\text{C}$ $p=4.6 \text{ mm}$					
36.7	242	77	vw	vw	
35.9	252	87	vw	vw	
31.4	308	143		vw	0+143 ?
24.4	395	230	vw		0+744-513 ?
23.7	404	239	w	nwr	0+239
17.5	482	317	vwd		0+744-2x214 ?
16.7	492	327		vw	
15.8	504	339	vwd		
$t=20^{\circ}\text{C}$ $p=4.6 \text{ mm}$					
15.1	513	348	wd	w	0+461-109
14.1	535	370	vw	vw	
08.4	598	433		vw	0+943-513 ?
06.2	626	461	nwd	ns	0+461
03.1	665	500	vwd	w	

Tablo III (continued)

λ (Å)	ν (cm ⁻¹)	$\nu - \nu_{0-0}$	Intensity		Assignment
$t=0^{\circ}\text{C}$ $p=1.1$ mm					
00.6	696	531	vw	w	0+744-214 ? 0+531 ?
2798.2	726	561		vwd	0+744-182 ?
92.9	794	629		vw	0+744-109
84.0	909	744	wdr	sr	0+744
78.3	982	817		w	
68.6	36108	943	vwd		0+943
65.2	153	988	vwd		0+744+239 0+988 ?
56.6	265	1100	vwd		0+744+461-109 0+1100
$t=-10^{\circ}\text{C}$ $p=0.6$ mm					
48.5	372	1207	wdr	vwd	0+744+461
41.2	470	1305	vwd		0+2x744-182
35.4	546	1381	vwd		0+2x744-109 0+3x461
27.6	651	1486	vwd	vwd	0+2x744
21.0	740	1574	vwd		
14.0	835	1669	wd	wd	
$L=14$ cm $t=10^{\circ}\text{C}$ $p=2.2$ mm					
09.6	917	1752	vwd	vwd	
02.6	37012	1847	vwd	wd	0+2x744+461-109 0+4x461 ?
2695.9	105	1940	wd	wd	0+2x744+461

Table III (continued)

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu - \nu_{\text{O-O}}$	Intensity		Assignment
88.3	209	2044	vwd	vwd	$0+3\times 744+182$
82.3	293	2128	wd	vwd	$0+3\times 744+109$
74.0	386	2221	wd	vwd	$0+3\times 744$
67.9	472	2307	wd	vwd	$0+5\times 461 ?$
62.0	554	2389	wd		
50.4	719	2554	vwd		
40.8	856	2691	wd		$0+3\times 744+461$
34.6	946	2781	wd		

Table IV. Absorption bands in transition II of α -picolino.

λ (\AA)	ν (cm^{-1})	$\nu - \nu_{0-0}$	Intensity	Assignment
$L = 25 \text{ cm}$ $t = -15^\circ\text{C}$ $p = 0.7 \text{ mm}$				
2669	37450	-170	vw	
64	530	-90	w	
57	620	0	mw	0 - 0
14	38250 ?	630	m	
2601	430 ?	810	s	0 + 810
91	580	960	vs	0 + 960
50	39200	1580	s	0 + 2 x 810
2531	500	1880	s	0 + 2 x 960
2493	40100 ?	2480	mw	0 + 2 x 810 + 960 ?

Table V. Absorption bands of transition II in β -picolino.

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	Intensity	$\nu - \nu_{0-0}$	Assignment	$\nu - \nu_{0-0}$	Assignment
L=10 cm t=5°C p=1.6 mm						
2741	36475	w	-905		0'	0-0'
32	585	vw	-795	Transition I ?	110	
28	645	vw	-735	Transition I ?	170	0'+170
21	745	mw	-635	Transition I ?	270	0'+460-190
16	800	mw	-580	Transition I ? 0-3x190	325	
07	935	ms	-445	0-445 ?	460	0'+460
02	995	w	-385	0-2x190	520	
2695	37100	w	-280		625	0'+170+460
88	190	ms	-190	0-190	715	
74	380	s	0	0-0	905	0'+2x460
63	540	ms	160	0+160 0+600-445?	1065	
47	770	n	390	0+(390)	1295	0'+460+1020-190
32	980	ms	600	0+600	1505	0'+460+1020
25	38090	mw	710	0+710	1615	
18	180	s	800	0+800 0+1020-190	1705	
09	320	vs	940	0+940	1845	
03	400	vs	1020	0+1020	1925	
2594	540	n	1160	0+160+1020 0+160+940	2065	
79	760	mw	1380	0+(390)+940 0+(390)+1020	2285	0'+460+2x1020-190
65	970	n	1590	0+600+940 0+600+1020	2495	0'+460+2x1020

Table V. (continued).

λ (Å)	ν (cm ⁻¹)	Intensity	$\nu - \nu_{0-0}$	Assignment	$\nu - \nu_{0-0}$	Assignment
51	39190	ms	1810	0+800+1020 0+2x1020-190	2715	
43	310	s	1930	0+2x940 ? 0+940+1020	2835	
28	540	n	2160	0+160+2x1020	3065	
14	760	n	2380	0+(390)+2x940 0+(390)+2x1020	3285	0+460+3x1020-190
02	960	n	2580	0+600+2x940 0+600+2x1020	3485	0+460+3x1020

Table VI. Absorption bands of transition II in γ -picoline.

λ (Å)	ν (cm ⁻¹)	$\nu - \nu_{0-0}$	Intensity	Assignment
$L = 14$ cm $t = 100^\circ$ $p = 2.25$ mm				
2616	38220	-100	mw	
2609	320	0	m	0-0 ?
92	570	250	m	
69	920	600	ms	0+600
48	39240	920	s	0+920
31	500	1180	s	0+1180; 0+2x600
2512	800	1480	ms	0+600+920
92	40120	1800	ms	0+2x920
74	410	2090	m	0+920+1180; 0+2x600+920
30	41140 ?	2820	m	
2417	360 ?	3040	mw	0+2x920+1180 ?

Beckman spectrophotometer in this laboratory do not show the two absorption regions separated as in the vapor. He found however, that the tail end of the absorption on the long wavelength side "disappears" in ethanol solutions of the picolines and also pyridine. (see also ref. 8). These observations in solution spectra and the fact that two absorption regions of different character occur in the picoline vapor spectra suggest the existence of two close-lying levels also in pyridine. Kasha,²¹ from research on halogenated pyridines and on pyridine in condensed systems has also come to this conclusion. A re-examination of Sponer and Stücklen's plates confirms the possibility of two levels and a rough estimate would place the beginning of the second transition around 38350 cm^{-1} .

It is obvious from these findings that the interpretation of the picoline spectra must follow, in general, the same pattern as that of the pyridine spectra. This necessitates reconsidering the previous interpretation of sharp pyridine bands as A_1-B_1 transition. It has been suggested by Kasha²¹ that excitation of an sp^2 electron of the nitrogen atom into the first unfilled π orbital of the pyridine ring causes the occurrence of system I. ($n-\pi$ transition) It is then logical to assign the diffuse bands to type II in the picolines to the A_1-B_1 transition ($\pi-\pi$ transition) resulting from the $2p\pi$ electrons of the ring. Since the sp^2 orbitals are symmetric to the molecular plane, the corresponding single electron levels are of type a_1 and b_1 . Excitation of an a_1 electron into the two lowest empty π orbitals of symmetry types b_2 and a_2 gives molecular levels B_2 and A_2 as lowest excited singlet states. This order is obtained by using the simplest molecular orbital calculation for the π electron orbitals neglecting

21. M. Kasha, Discuss. Far. Soc. 9, 14 (1950).

overlap and electronic repulsion²². In Kasha's scheme of levels the A_2 is the lowest excited singlet state of pyridine; then follow the B_2 and the B_1 which is the upper state of the II spectra. An A_1-B_2 transition is allowed with a transition moment perpendicular to the molecular plane. We shall see later that the analysis suggests an order of the A_2 and B_2 levels in agreement with the simple calculations. This may be taken as an indication that inclusion of refinements in the calculation of the π orbitals will not reverse the order given by the crude treatment.

It should be added that the level notation used here applies strictly to pyridine only, and to γ -picoline if the CH_3 group is regarded as one atom. α -Picoline and β -picoline belong, even if the CH_3 groups are taken as one-atom substitutions, to group C_s . The symmetry classes A_1 and B_1 of group C_{2v} go over into the class A' for C_s , and the two transitions involving the sp^2 electrons become $A'-A''$ transitions with the moment perpendicular to the molecular plane. The appearance of the electronic spectra and a comparison of the different Raman spectra indicate that α -picoline and β -picoline also conform spectroscopically to C_{2v} symmetry to a rather fair approximation.

Transition II in the Region 2600 Å⁰

From the description (diffuseness and position) given before, the II spectra of the four compounds appear to fall into two groups corresponding to their different symmetries: pyridine and γ -picoline (C_{2v}), and α - and β -picoline (C_s).

α -Picoline. Estimated band positions in spectrum II of α -picoline are listed in Table IV. This spectrum is so diffuse (Fig. 4) that no individual bands can be distinguished clearly except the three in the

22. Gertrud P. Nordheim and H. Sponer, J. Chem. Phys. 20, 285 (1952).

first group. The separation of the order of 1000 cm^{-1} between the maxima of successive groups correspond presumably to progressions of the analogue of the totally symmetric carbon ring vibration in benzene. The strongest band of the first group, at 37620 cm^{-1} , is taken as the 0-0 band. Another symmetric ring vibration is probably represented in the separation 810 . The bands on the long wavelength side of the 0-0 band must correspond to 1-1 transitions of low-lying vibrations.

β - Picoline. The only transition II spectrum whose band structure is sufficiently discrete to permit of any detailed analysis is that of β -picoline (Fig. 4, Table V). Even in this case the interpretation is not satisfactory. If the strongest band in the first group, at 37380 cm^{-1} , be designated 0-0, most of the strong bands can be accounted for by progressions of frequencies of about 940 and 1020 cm^{-1} superimposed upon the 0-0 transition and upon the following vibrational frequencies in the excited state: 160 , 390 , 600 , 800 cm^{-1} . The 940 and 1020 probably correspond to the strongly polarized Raman frequencies 993 and 1034 cm^{-1} in the ground state which quite likely represent symmetric carbon ring vibrations. If the first band on the long wavelength side of the 0-0 band at 37190 cm^{-1} , is interpreted as arising from the vibration of approximately 190 cm^{-1} (Raman value 198), then the 160 cm^{-1} difference may correspond to the same vibration in the excited state. This would place the 1-1 transition of this vibration about 30 cm^{-1} to the red from the main bands. Since the widths of most bands are of the order $30 - 60\text{ cm}^{-1}$, it is quite possible that these 1-1 transitions contribute at least partially to the broadness of the bands.

The $0 + 600\text{ cm}^{-1}$ difference (band 37980) has about the same in-

tensity as the 0-0 band, and has a breadth and uniformity of intensity which suggests that it may consist of two close-lying bands. The band may correspond in the upper state to the 624 cm^{-1} level observed in the Raman spectrum, but this possibility must be regarded as uncertain. It is very probable that the Raman lines 624 and 535 cm^{-1} correspond to the degenerate E_g^+ 606 carbon vibration in benzene, and one would expect that if one component appeared in the excited state of β - picoline the other would appear also. But the 390 cm^{-1} difference seems too low to be correlated with 535 in the ground state.

The 800 cm^{-1} difference (band 38180) may be attributed to a ring vibration in the upper state in which the substituent is strongly participating. An alternative explanation is possible as a superposition and given in Table V.

Perhaps the greatest objection to the foregoing interpretation is that it offers no explanation of the prominent bands at 36475 and 36935 cm^{-1} . If instead of 37380 the band at 36935 cm^{-1} is itself taken as the 0-0 band, most of the system can be accounted for by progressions of about 940 and 1020 cm^{-1} superimposed upon the frequencies: $445, 605, 835, 1045\text{ cm}^{-1}$. The band at 37380 becomes $0 + 445$. This frequency may then represent the vibration which has the Raman value 535 cm^{-1} . The fact that its intensity is remarkably greater than that of the 0-0 band may result from the Franck-Condon principle. In that case, however, a progression of one, two, and possibly three times 445 would be expected, whereas only the single 445 cm^{-1} difference appears. 605 cm^{-1} may be reasonably identified with the 624 vibration in the lower state, in the same manner as before. The 255 cm^{-1} difference agrees with $445 - 190$. The analogue of the 190 cm^{-1} vi-

bration in the upper state is possibly represented by the 165 cm^{-1} difference (band 37100). It is very difficult to account for the differences of 835 (band 37770) and 1045 (band 37980). Altogether, the first interpretation — taking the 0-0 band at 37380 cm^{-1} — seems preferable.

Still another interesting possibility remains. According to Kasha²¹ two overlapping electronic transitions occur in pyridine and its monohalogenated derivatives very close together in the region of 2600 Å . This view is based on the assumption that the A_1-B_2 transition (Kasha's scheme) occurs only slightly below the benzene-like A_1-B_2 transition discussed here. No evidence of a second transition in this region was found in the spectrum of α -picoline. Its occurrence cannot be ruled out, however, in β -picoline. Careful examination of this spectrum in plates and enlarged prints reveals that the band at 36475 cm^{-1} does not look like the bands of transition I, while certain weak bands at shorter wavelengths — e.g., those at 36585, 36745, and 36800 cm^{-1} — do resemble the bands of spectrum I. The band at 36475 actually resembles that at 36935 cm^{-1} , except that it is weaker.

If it is assumed that 36475 is the 0-0' band of a second electronic transition, the prominent band at 36935 cm^{-1} then becomes $0' + 460\text{ cm}^{-1}$ and may be correlated with the 535 cm^{-1} vibration in the lower state. This vibration, with the lower-state vibration of 190 cm^{-1} and an upper-state vibration of about 1020 cm^{-1} , accounts for several bands which are not included in the scheme based on a 0-0 band at 37380 cm^{-1} , and duplicates some which are (Table V). Because of accidental near coincidence between the two proposed systems and the diffuseness of the bands, it is not possible to propose the existence of two transitions in the II region with entire confidence, although

it is considered quite likely.

It should perhaps be mentioned that the band at 36475 can be related to the O-O band at 37380 by the assignment $0-190-714\text{ cm}^{-1}$. No weight is placed on this interpretation, however, and no similar interpretation of the band at 36935 is possible.

It seems desirable to emphasize again that the analysis of the bands in region II in β -picoline suggested here is necessarily tentative. It has been mentioned in some detail because it is important to establish definite proof whether two superimposed transitions occur in region II or not. We shall come back to this question after the analysis of transition I has been taken up.

γ -Picoline. The bands of transition II in γ -picoline are so few and so diffuse that a systematic analysis of them does not carry much weight. It is believed that probably the band at 38320 cm^{-1} is the O-O band. With this assumption the assignment scheme in Table VI may be obtained as a possible one. This interpretation, like the intensity considerations mentioned earlier in this section, indicates a marked shift of the γ -picoline II spectrum to the violet as compared with α and β -picoline. This shift, and the lower intensity of the γ -picoline II spectrum are contrary to the usual characteristics of para-substituted benzenes. We shall come back to it in a later section.

Because of the diffuseness of the γ -picoline spectrum in both transitions I and II, it is impossible to judge whether a second electronic transition occurs in the short wavelength II region.

Transition I in the Region 2800 Å

In considering the analyses of the I spectra it will be recalled that these spectra are expected to arise from the excitation of an sp^2 electron localized on the nitrogen into the first non-bonding π ring orbital. On the basis of this theory the I spectra represent either a forbidden A_1-A_2 transition or an allowed A_1-B_2 transition with a moment perpendicular to the molecular plane. Consequently, the analyses of the spectra should lead to a decision between these possibilities.

Before going into details, it will be mentioned that nothing could be found in the structure of these spectra that would suggest a forbidden transition. The detailed analyses will be found rather to provide support for the assumption of an A_1-B_2 transition. The fact that the I spectra are allowed and yet are of markedly lower intensity than the II spectra is noteworthy. A transition depending upon a perpendicular moment will be weak because the overlapping of the π ring orbital and the localized σ orbital is small.

The characteristic narrowness of the bands in the I spectra may also be related to an A_1-B_2 transition. In benzene, whose rotational levels may be treated as those of a symmetric top, all strong bands should be perpendicular bands²³ (change of electric moment \perp to the figure axis.) In pyridine and in γ -picoline the figure axis lies in the molecular plane and goes through the N atom and the para carbon atom. The transition moment, being perpendicular

23. H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, J. Chem. Phys. 7, 207 (1939).

to the molecular plane, is perpendicular to the figure axis as in benzene. Bands involving symmetric vibrations should then be perpendicular bands. However, if one considers, in good approximation, pyridine as a symmetric top like benzene³, the z axis may be taken as the figure axis and the principal moment of inertia is the one about this axis. Bands involving symmetric vibrations become parallel bands in this treatment whereas they are perpendicular bands in benzene. The difference stems, of course, from the different origin of the two spectra, one having a transition moment perpendicular and the other parallel to the molecular plane. The parallel bands of a symmetric top molecule in the infrared have simpler appearance than the perpendicular bands. They have extremely narrow intense qQ branches. Little is known about their structure in electronic bands of polyatomic molecules, but in the case of the strong benzene bands (theoretically perpendicular) it was noted²⁴ that the relation between the variation in spacing of the rotational lines and the change in moments of inertia would be the same if the bands were interpreted as parallel bands. In the discussion of the pyridine spectrum³ it was pointed out that if the moments of inertia stay very nearly the same in the upper and lower states of the transition, the qQ branch will be intense and narrow, while the P and R branches may extend so far to each side that their intensities decline to negligible values before a head is reached. This latter effect, occurring in suitable degrees, could account for the shading and fuzziness at the edges of most bands. If the transition moment is perpendicular to the molecular plane as is requi-

24. A. Turkevich and M. Frod, Rev. Mod. Phys. 14, 246 (1942).

red in an A_1-B_2 transition, the symmetry of the charge distribution in the plane will not have changed, although the electronic wavefunction of the excited state will be somewhat extended. Nearly equal moments of inertia in the two electronic states will require that the potential minima of bands involving symmetrical vibrations are approximately above one another. Equal equilibrium positions in the combining states is always most probable for non-totally symmetric vibrations.

Assuming an A_1-B_2 transition as a working hypothesis, one might expect in the I spectra few and relatively short progressions of totally symmetric vibrations. Furthermore, singly excited α_2 and β_2 vibrations in pyridine and γ -picoline, which produce vibrational moments in the plane of the ring, should appear with intensities comparable to those of the α_1 allowed vibrations which accompany the weak pure electronic transition in the z direction. But singly excited β_1 vibrations, prominent in A_1-B_1 transitions, should be excluded. In α - and β -picoline, however, the reduction of C_{2v} symmetry to C_s produces allowed electronic transitions only.

It will be noted as the analyses are developed that the I spectra of α - and β -picoline, particularly the former, resemble that of pyridine, while the spectrum of γ -picoline is similar in some respects to that of toluene.²⁵

γ -Picoline. The analysis of the γ -picoline I spectrum is taken up first, because it is the least complex and offers a better

25. N. Ginsburg, W. W. Robertson and F. A. Matsen, J. Chem. Phys. 14, 511 (1946).

opportunity for unambiguous interpretation than do the less symmetric α - and β -picolines. It is unfortunate that no Raman data are available for γ -picoline. The observed spectrum is, however, sufficiently simple that it is relatively easy to isolate a few fundamental frequencies upon which an internally consistent analysis can be developed.

The strong doublet at 35165 cm^{-1} is taken as the 0-0 band. The basic pattern of the γ -picoline I spectrum is a series of dispersed groups; each of these consists of three prominent frequencies superimposed upon a progression of 744 cm^{-1} . The lower state of this vibration appears in the band at -800 cm^{-1} . The corresponding frequencies in toluene are 751 and 785, and in para-xylene they are 775 in the upper state²⁶ and 829 in the lower state. Although the precise nature of these frequencies is not certain, they do involve a strong participation of the substituent in the motion by either lowering the value of the benzene "breathing" vibration²⁷ or by actually representing the $-\text{C}-\text{C}-(\text{H}_3)$ valence vibration.²⁸ A slight preference is given here to the first alternative. The three observed bands of the 744 progression are strong and diffuse, and are degraded to the red similarly to the bands in the spectra of substituted benzenes. Observation of higher members is rendered impossible because of the increasing intensity of the continuous background. The 744 bands form the only progression that

26. C. D. Cooper and M.L.N. Sastri, J. Chem. Phys. 20, 607 (1952).

27. K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. 65, 803 (1943).

28. K. W. F. Kohlrausch and Associates, Monatsh. Chem. 72, 268 (1939); 74, 175 (1942); 76, 200 (1947).

could be established with certainty. This fact and the diffuse quality of the bands indicate that during the transition a slight change takes place of the internuclear distances involved in this vibrational mode.

The 239 cm^{-1} frequency is ascribed tentatively to either an α_2 or β_2 carbon vibration. The corresponding frequency in the lower state is uncertain.

The $461\text{--}513\text{ cm}^{-1}$ pair is considered as the α_1 component resulting from the E^+_g 606 carbon vibration in benzene. Both values agree closely with those in toluene as might be expected for the vibrational mode concerned. The 461 frequency occurs superimposed upon the 0-0 frequency and upon each member of the 744 progression; but it is not certain that it forms itself a progression.

The β_1 component derived from the E^+_g 606 benzene vibration is missing from the I spectrum of γ -picoline. A weak band at $0 + 531\text{ cm}^{-1}$ may possibly represent it in the upper state, but the low intensity of this band and the absence of the corresponding vibration from the lower state indicate that, if any representation of the β_1 vibration is present at all, it must arise from a very weak moment. This finding is in accord with the hypothesis of an $A_1\text{--}B_2$ transition. The presence of the CH_3 group may cause a sufficient deviation from C_{2v} symmetry to permit such a weak transition of an otherwise forbidden vibration.

The third frequency which is found superimposed upon the 744 cm^{-1} terms is a difference of 109 cm^{-1} which is taken to be a 1-1 transition of a vibration which is not identified explicitly. The 109 difference frequency is also found in combination with the 0-0 transition and with the 461 frequency.

The frequencies which have been mentioned account for nearly all of the more prominent features of the spectrum. Of the numerous weak bands remaining, several probably represent fundamental frequencies; but the assignments are made chiefly by analogy, and lack supporting combinations.

The band at $\sim 214 \text{ cm}^{-1}$ probably corresponds to the 204 and $196 - 208 \text{ cm}^{-1}$ Raman frequencies in α - and β -picoline, and should appear in the Raman spectrum of γ -picoline. The band at 143 cm^{-1} is a likely upper-state analogue.

Weak bands at $0 + 943$ and $0 + 988 \text{ cm}^{-1}$ probably represent a_1 carbon vibrations. The band at $0 + 1100 \text{ cm}^{-1}$ possibly includes the 0-1 term of a fundamental frequency superimposed upon the known combination $744 + 461 - 109 \text{ cm}^{-1}$. The 1100 frequency agrees closely with similar frequencies in α - and β -picoline.

Several more uncertain assignments have a question mark in Table III.

It should be mentioned that the 0-0 and the $0 - 513 \text{ cm}^{-1}$ bands are very sharp doublets of 4 cm^{-1} separation. No other bands appear to have this doublet structure, and no explanation of the doubling is apparent.

α - and β -Picoline. It is convenient to treat the I spectra of α - and β -picoline in a single discussion, because of their marked similarities. Because of the low symmetry of these molecules, all their spectra will actually represent allowed transitions $A' - A''$ with a moment perpendicular to the molecular plane. (See previous discussion). Single excitation of a'' vibrations will produce bands in which the transition moment is in the ring plane. The symmetry of these vibrations corresponds to the α_2 and β_2 vibrations of point group C_{2v} , and these are the vibrations that were believed to account

for some of the weaker bands in the γ -picoline spectrum. Hence the I spectrum of α - and β -picoline will be richer in bands than that of the γ -isomer, just as the ortho and meta spectra of disubstituted benzenes have more bands than the corresponding para compound. Although the vibrations fall, in the strict sense, into two classes only, one would expect from what has been said before that those will occur with more prominence than were recognized in the γ -spectrum. In spite of this aid it was found that the number of numerical coincidences of interpretation was so great that many assignments must be considered as tentative.

In α -picoline the sharp band at 34753 cm^{-1} was taken as O-O band. In β -picoline the close pair $34684/97$ contains in all probability the O-O transition. Here the lower value was chosen for the calculation because of a rather consistent fit with Raman values. As may be seen from Table II, there appear in the spectrum several other "doublets" with a separation of $12 - 14\text{ cm}^{-1}$. The 544 cm^{-1} frequency in the upper state, which is the outstanding feature of the pyridine spectrum, is similarly prominent in α -picoline but forms a less clearly defined progression in the β -spectrum. If it is associated in each case with a vibration of 628 cm^{-1} in the ground state (depolarized Raman line), then the $544, 628\text{ cm}^{-1}$ pair would represent the β_1 component derived from the ξ_g^+ 606 cm^{-1} carbon vibration in benzene. The fact that it is depolarized in Raman spectra of α - and β -picoline, even though the class β_1 of group C_{2v} goes into the totally symmetric class α' in C_8 , indicates that the effect of the CH_3 substitution in destroying the C_2^y axial symmetry of pyridine is incomplete. Nevertheless, it may be sufficient to make allowed the transition of the β_1 vibra-

tion which is forbidden in γ -picoline if this is treated as a C_{2v} molecule. The association of the 544 and 628 cm^{-1} frequencies is supported by the occurrence of 84 cm^{-1} differences in both spectra. Although all symmetry requirements are formally met, the β_1 vibrational bands should occur with low intensity because of the "remembrance" being originally forbidden transitions. This is not the case. It is therefore of interest that another assignment is possible. The 544 may namely correspond to the vibrations of 545 and 551/35 in the lower states of α - and β -picoline, respectively. Raman data indicate that these vibrations are totally symmetric; they are believed to arise from the α_1 component of the E_g^+ 606 cm^{-1} vibration in benzene. In fact, this interpretation, which is preferred here, fits in better than the first one with results in the spectrum of pyridine, where a long progression of 542 steps has been found and assigned to the α_1 component. The difficulty that in β -picoline there is definite evidence of an upper-state 499 cm^{-1} vibration, may be met by pairing it with the 515 in the lower state. Both α - and β -picoline have an upper-state vibration of about 580 cm^{-1} occurring weakly which then might be paired with the 628 cm^{-1} .

Polarized Raman lines have been reported at 801 and 813 in α -, and at 714 and 800 cm^{-1} in β -picoline.¹¹⁻¹³ The same frequencies were found in the ultraviolet absorption spectrum. One of these frequencies will correspond to the analog of the benzene "breathing" vibration as discussed for γ -picoline. In α -picoline, it is possibly represented in the upper-state by the band at $0 + 736 \text{ cm}^{-1}$, and in β -picoline, by a strong band at $0 + 802 \text{ cm}^{-1}$. A short progression of 269 cm^{-1} is superimposed upon this transition. The

802 band consists of a closely spaced sharp doublet from which diffuse wings are degraded unequally to either side; they appear to end abruptly at a low intensity and do not form a head.

Several low-lying fundamental frequencies are found which are difficult to interpret definitely. In α -picoline some almost identical separations which probably represent fundamental frequencies are observed to either wavelength side from the 0-0 band. These pairs have been noted: 207, 204; 355, 358; 544, 545 cm^{-1} . Yet there remains a 120 cm^{-1} frequency which, if paired with 204 cm^{-1} in the lower state would account for the 1-1 difference of 84 cm^{-1} . This difference could possibly be interpreted as the twofold excitation of a 42 cm^{-1} difference occurring a few times in α -picoline; but the predominance of the 84 over the 42 difference, its likely origin in the 120-204 difference, and other internal evidence argue for two distinct frequency differences. In β -picoline no such closely-matched pairs occur. Here, 158 and 198 cm^{-1} are paired, and their difference may account for the prominent 1-1 difference of 40 cm^{-1} which is observed singly and in progressions to the red from many strong bands. The 84 cm^{-1} difference may result from pairing the lower state frequency of 215 with the upper ^(state) frequency of 131 cm^{-1} . The 207 and 269 cm^{-1} upper state vibrations of α - and β -picoline, respectively, are quite likely of type α_2 or β_2 (α''), and hence their single excitation would produce a moment in the molecular plane. This fact may account for the prominence of the respective bands.

Frequencies of 900-1000 cm^{-1} which produce strong bands in the II transitions and in benzene and its monoderivatives, give rise to weak inconspicuous bands only in the I transition under discussion.

Their assignment to particular modes of vibration is uncertain and will therefore not be discussed in detail.

A few words may be added on the origin of the bands in the II region of β -picoline, which were tentatively assigned to another transition, besides the A_1-B_1 (or A^1-A^1) containing the main groups. As mentioned, this other transition may belong to the second excitation of an sp^2 electron from the nitrogen. And as such, it should be of type A^1-A^1 , but should resemble a forbidden transition A_1-A_2 . The very tentative and incomplete analysis is not in contradiction to this assignment, but it would be more interesting and important if corresponding bands could be identified in pyridine and γ -picoline where the systems would be more of type A_1-A_2 . They could appear through interaction of β_1 and β_2 vibrations. Excitation of β_2 vibrations should be more effective because it would produce a transition moment in the molecular plane in the same direction as in the overlapping A_1-B_1 π electron transition. In fact, because of the proximity of the two transitions, they should be of comparable intensities,²⁹ as is the case in β -picoline.

Summary and Conclusions

The evidence summarized in the last section indicates that the question of symmetry of the electronic I transitions cannot be considered settled on the basis of the analyses alone. Among these, the more definite findings in the study of the γ -picoline spectrum carry more weight than do the less definite results in the cases of α - and β -picoline. It is evident, however, that the observations as to narrowness of bands, shortness of progressions, and the

29. G. Herzberg and E. Teller, Z. phys. Chem. B 21, 410 (1933);
H. Spöner and E. Teller, Rev. Mod. Phys. 13, 75 (1941).

operation of symmetry selection rules upon various classes of vibrations, together with the low intensity and allowed character of the transition, all constitute a strong argument for B_2 symmetry in the electronic excited state.

Another argument in favor of the interpretation may be raised from a comparison of the intensities of the I transition of pyridine and the picolines with those of the diazines which have been studied by Halverson and Hirt.³⁰ If the I spectra are allowed transitions due to the excitation of a nonbonding electron from the nitrogen, then the corresponding spectra in the diazines should be about twice as intense as the I transition in pyridine or the picolines. Comparison of the f values of the I transitions in the latter substances with those derived from the published diazine absorption curves shows that this is indeed the case.

The electronic transitions in pyridine and the picolines discussed here have been summarized in Table VII. As has become apparent from the text, the values for transitions II are considered more liable to possible future changes than those for transitions I. Still more uncertain is the analysis of the A_1-A_2 system of β -picoline. The steep absorption gradient between the I and II spectra makes it very difficult to establish with certainty another electronic transition in this region. On the other hand, the very existence of this gradient and the diffuseness of transitions II make overlapping of another and possibly more transitions in this region likely.

It may be seen from the last table that the red shift of the ${}^1A_1-{}^1B_2(n-\pi)$ transition is smaller than that of the ${}^1A_1-{}^1B_1(\pi-\pi)$

30. F. Halverson and R. C. Hirt, J. Chem. Phys. 19, 711 (1951).

transition for all molecules except for γ -picoline. Accordingly, the difference between the excited levels 1B_1 - 1B_2 decreases from pyridine to β -picoline. Of course, it should be remembered that the location of the 1A_1 - 1B_1 transition in pyridine is a rough estimate only. In γ -picoline both spectra shift to the violet, the II transition twice as much as the I transition, so that the difference 1B_1 - 1B_2 increases again and comes close to that in pyridine. In regard to intensities, the A_1 - B_2 transition is the weakest in γ -picoline and the A_1 - B_2 is just a little stronger in γ -picoline than in the other two isomers.

For completeness, the two singlet-triplet transitions of pyridine have been added which were recently studied by Reid.³¹ However, the assignments of the system to symmetry types are reversed here. The 31000 cm^{-1} intercombination system, which resembles the 1A_1 - 1B_2 transition, is connected here with the unpaired non-bonding electrons on the nitrogen. It is at least 10^3 times weaker than the corresponding singlet system. The second intercombination system at 25500 is still weaker by another factor 10^2 - 10^3 . It resembles transition II in its diffuseness and may be regarded as a π - π transition. This means, that while the singlet and triplet B_2 levels lie only about 4000 cm^{-1} apart and actually overlap a little, the singlet and triplet B_1 levels are more than 12000 cm^{-1} apart and lie in different spectral regions. It is hoped to treat later the energy and intensity relations in these molecules.

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31. C. Reid, J. Chem. Phys. 18, 1673 (1950).

Table VII. Electronic transitions (in cm^{-1}) in pyridine and the picolines in the near ultraviolet.

Molecule	$\left. \begin{array}{l} 1A_1 \rightarrow 1B_2 \\ 1A' \rightarrow 1A'' \end{array} \right\} \left. \begin{array}{l} sp^2 \sigma \\ \text{electron} \end{array} \right\}$	$\left. \begin{array}{l} 1A_1 \rightarrow 1B_1 \\ 1A' \rightarrow 1A' \end{array} \right\} \left. \begin{array}{l} p\pi \\ \text{electron} \end{array} \right\}$	difference	$\left. \begin{array}{l} 1A_1 \rightarrow 1A_2 \\ 1A' \rightarrow 1A'' \end{array} \right\} \left. \begin{array}{l} sp^2 \sigma \\ \text{electron} \end{array} \right\}$	$3A_1 \rightarrow 3B_2$ sp ²	$3A_1 \rightarrow 3B_1$ p π
Pyridine	34769	(38350)	(3581)		30876	25500
α -Picoline	34753	37620	2867			
β -Picoline	34684	37380	2696	(36475?)		
γ -Picoline	35165	38320	3155			